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(54) Hydrophilic polyurethane/polyurea sponge

Hydrophiler Polyurethan/Polyharnstoff-Schwamm

Eponge hydrophile de polyuréthane/polyurée

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Description

Technical Field

This invention relates to a hydrophilic polyurethane/polyurea sponge and a process therefor. The synthetic sponge is useful in home and industrial cleaning applications.

Background Art

Cellulose sponges are in wide use for many cleaning applications. The process for providing cellulose sponges is environmentally disadvantageous due to toxic gaseous and liquid by-products.

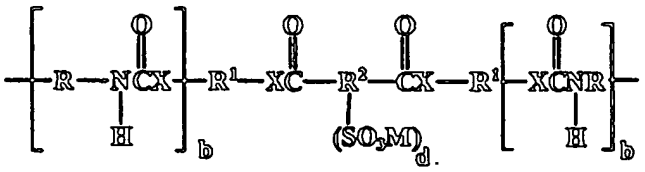
Polyurethane sponge materials have been known and utilized for a long time. Most of these sponges are synthesized from isocyanate terminated polyethyleneoxide, polypropyleneoxide, polyesters, or combinations thereof. Coreactants are usually polyols or polyamines of similar polymeric backbones. Water is also used as a coreactant which generates a blowing agent (i.e. carbon dioxide) in addition to generating a crosslinked system. The majority of these materials produce a sponge material with little hydrophilic character (moderate bulk hydrophilicity, but poor surface properties), and few of the characteristics associated with a cellulose sponge. Materials which are claimed to be hydrophilic usually contain a sacrificial hydrophilic compound or have excessive swell (in excess of 50%).

Isocyanate terminated sulfopolyethyleneoxide prepolymers have been described in US-A-4,746,717 Other sulfonated prepolymers for foam applications are described in U.S. Patent No. 3,988,268. The use of sulfonated urethanes have otherwise been mainly restricted to the synthesis of water-soluble or water-dispersible materials, e.g. U.K. Patent No. 1,483,687. Prepolymers based on isocyanate-terminated polyethyleneoxide are described in U.S. Patent Nos. 4,160,076; 4,384,050; 4,384,051; and 4,377,645.

EP-A-000,724 discloses a hydrophilic water-absorbing sponge comprising a polymer of urea and/or urethane and incorporating at least one sulphonate equivalent per 20,000 molecular weight units.

Summary of the Invention

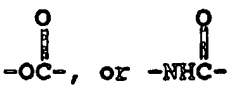
Briefly, the present invention provides a hydrophilic water-absorbing sponge as in the above summary of EP-A-000,724 characterised in that the polymer comprises a plurality of units having the formula:



wherein

R is an organic group having a valence of 2, 3 or 4 selected from linear and branched aliphatic groups having 2 to 12 carbon atoms, and 5- and 6-membered aliphatic and aromatic carbocyclic groups having 5 to 50 carbon atoms;

each R^1 is independently a linear or branched organic group having a valence of(b + 1) consisting of a chain of up to 110 carbon atoms in units selected from linear groups C_nH_{2n} and C_nH_{2n-2} in which n is 2 to 12, 5- or 6-membered carbocyclic groups, and aromatic groups of 5 to 20 carbon atoms, which are separated by ether oxygen atoms, or

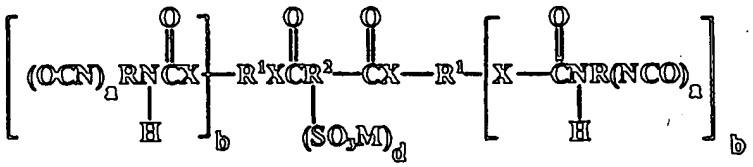


the linear or branched organic group having a molecular weight of up to 2000, wherein b is an integer of 1, 2 or 3; and R^2 has a valence of d + 2 and is an arenepolyyl group (polyvalent arene group) having 6 to 20 carbon atoms or an alkanepolyyl (polyvalent alkane) group having 2 to 20 carbon atoms,

wherein d is a number 1, 2 or 3,
X is independently -O- or -NH-, and
M is a cation.

Preferably, the polymers contain one sulfonate equivalent per 3,000 to 10,000 molecular weight units.
In another aspect, this invention provides a method of preparing a sponge comprising the steps of:

(a) providing an isocyanate-terminated sulfopolyurethane/urea comprising a compound having the formula



and, optionally, at least one of compounds having the formulae
$OCNR(NCO)_a$ and

wherein a is an integer of 1 to 3, b is an integer of 1 to 3, and R, R^1, R^2, X and M are as defined in claim 1;
b) reacting said sulfopolyurethane/urea with at least one of

(a) water, and
(b) at least one of a polyol or polyamine plus a blowing agent, and
c) isolating the resulting sponge,

said sponge incorporating at least one sulfonate equivalent per 20,000 molecular weight.

In many applications it is desirable for a sponge to resist excessive shrinkage upon drying. In particular, sponges which are laminated to abrasive scrubbing pads, which are commonly used for household and industrial cleaning, become unattractive and in some instances undergo adhesive failure of the laminate upon drying. Large variations in volume between the swollen and dry state of a sponge can be detrimental in such applications.

The sponges of the instant invention, surprisingly, are superior to cellulose-based sponges in that upon drying they exhibit considerably less shrinkage, i.e., 30%, 40%, or even up to 50% less shrinkage compared to cellulose-based sponges. The total water absorption and rate of water take-up is at least as good or better than cellulose-based sponges. Further, the wet wipe capability of the sponges of the instant invention is equal to that of cellulose-based sponges and is superior to that of natural sponges and known polyurethane sponges.

The preferred article of the invention has open cells which range in size from 3.0 cm to less than 1.0 micrometer, preferably 1.0 cm to less than 1.0 micrometer, has a dry density in the range of 0.03 to 0.1 g/cm^3 and preferably has a volumetric swell in water of less than 30%. The sponge is equal to or improves upon existing cellulose derived sponges in the following areas of performance: wet wipe, rate of water absorption, percent swell in water (reduced shrinkage upon drying), tensile strength, and toughness.

Further preferred features are defined in the dependent claims.

In this application

"sponge" means a porous, open-cellular mass capable of absorbing liquids, and is elastic and flexible when damp;
"flexible" means can be bent through an angle of 180° without cracking or breaking;
"wet wipe" means the ability of a damp sponge to remove water from a surface;
"aliphatic" means linear, branched, or cyclic unless otherwise stated;

"pendant" means suspended from the main chain (backbone) of the polymer;
"catenary" means in the main chain or backbone and not in a pendant or terminal group;
"sulfo" means a $-SO_3H$ group or a salt thereof;
"sulfocompound" means a compound containing a pendant sulfo group; and
"plurality" means a number of three or more.

DETAILED DESCRIPTION

The sponge of one embodiment of the invention comprises a polymeric 3-dimensional network and has an absorptive capacity of 10 to 50, preferably 10 to 30 grams of water per gram of dry sponge, and a rate of water absorption of 0.001 to 0.04 $g/cm^2/5$ seconds, a density in the range of 0.01 to 0.4 g/cm^3, preferably 0.03 to 0.1 g/cm^3, and a percentage volumetric swell in water of less than 50%, preferably less than 30%, and most preferably 15 to 25%, and wet wipe capacity of 85 to about 100%, and as noted above, has additional properties equal or better than those of cellulose and natural sponges. The sponge of the invention can be prepared by a process that is simpler than the process for preparing cellulose sponges, and does not produce large quantities of environmentally damaging by-products.

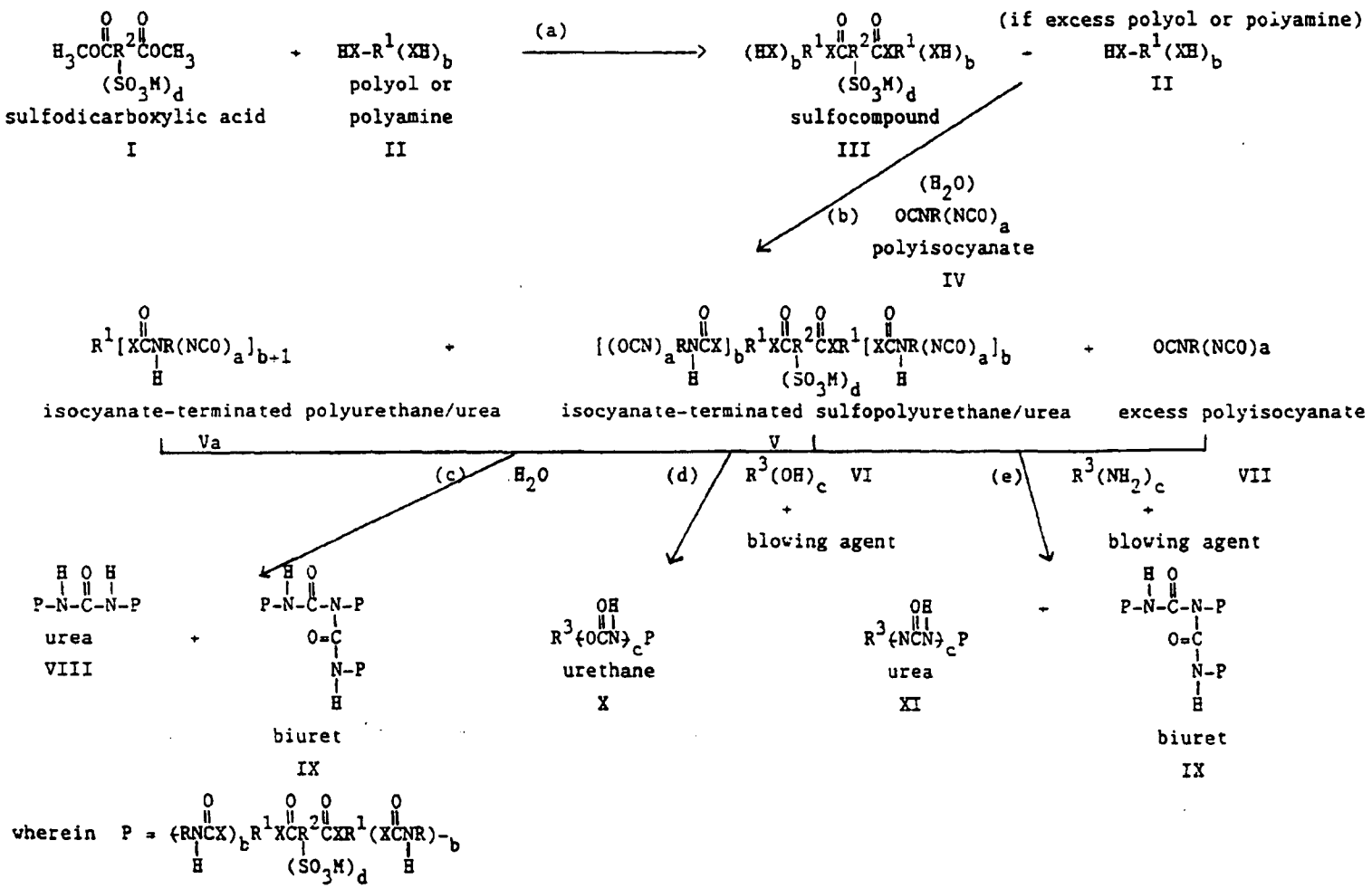
In the process of the invention the coreactant of step b) can for example include at least one of

a) 1 to 50 moles of water, and
b) about 0.8 to 1.2 moles of a polyol and/or 0.05 to 1.5 moles of a polyamine plus a blowing agent.

Preparation of an isocyanate-terminated sulfopolyurethane can for example involve an excess of polyisocyanate of Formula IV in the following FLOW CHART in the reaction with a sulfopolyol or sulfopolyamine in an amount up to about 100% excess (eg. up to about four moles of polyisocyanate per mole of sulfopolyol or sulfopolyamine). When such an excess is used the isocyanate-terminated sulfocompounds of Formulae V and Va in the following FLOW CHART mixed with excess polyisocyanate is obtained.

The process of the invention is depicted in the FLOW CHART below wherein R, R^1, R^2, R^3, X, M, a, b, c, and d are as defined above.

FLOW CHART


sulfodicarboxylic acid
I
polyol or polyamine
II
(a)
sulfocompound
III
(if excess polyol or polyamine)
II
(b)
(H2O)
polyisocyanate
IV
isocyanate-terminated polyurethane/urea
Va
isocyanate-terminated sulfopolyurethane/urea
V
excess polyisocyanate
(c)
H2O
(d)
VI
blowing agent
(e)
VII
blowing agent
urea
VIII
biuret
IX
urethane
X
urea
XI
biuret
IX
wherein P =

Preferably, the isocyanate-terminated sulfopolyurethane/urea of Formulae V is prepared by the reaction of one mole of sulfoarene or sulfoalkane dicarboxylic acid, Formula I, (or their esters prepared from an alcohol of low molecular weight, i.e. below about 94, their acid anhydrides, or their acid halides) with two to four moles of monomeric or polymeric polyol or polyamine of Formula II having (b + 1) groups selected from amino and hydroxyl groups forming a sulfopolyol or sulfopolyamine designated a sulfocompound having 2b hydroxyl and/or amino groups, wherein b is an integer of 1, 2, or 3. When more than two moles of monomeric or polymeric polyol or polyamine is used isocyanate-terminated polyurethane/urea of Formula V is also formed. The sulfocompound (Formula III) or the mixture of sulfocompound and compound of Formula Va is then caused to react with from 2b to up to 16b plus 8 moles of an organic polyisocyanate to form an isocyanate-terminated sulfocompound. As is known in the art, these reactions can be performed in the presence of a mercury, lead or tin catalyst such as dibutyltin dilaurate. Preferably, the catalyst is a tertiary amine, tricalcium aluminate, or the potassium salt of a molybdenum ester of triethyleneglycol as is disclosed in U.S. Patent No. 2,916,464. The preparation of the sulfocompound can be carried out by heating the reactants for about 2 to 20 hours, preferably 4 to 10 hours, at temperatures from 150 to 300°C, preferably 200 to 250°C, under reduced pressure or an inert atmosphere.

Polyols $(HO)_bR^1OH$ of Formula II, which can be aliphatic or aromatic polyols, useful in preparing the polyurethane/polyurea sponges of the invention can, for example, have a molecular weight of 62 up to 2000 and include, for example, monomeric and polymeric polyols having two to four hydroxyl groups. Examples of the monomeric polyols include ethylene glycol, propylene glycol, butylene glycol, hexamethylene glycol, cyclohexamethylenediol, 1,1,1-trimethylolpropane, pentaerythritol, and the like. Examples of polymeric polyols include the polyoxyalkylene polyols (i.e., the diols, triols, and tetrols), the polyester diols, triols, and tetrols of organic dicarboxylic acids and polyhydric alcohols, and the polylactone diols, triols, and tetrols having a molecular weight of 106 to about 2000. Examples of polymeric polyols include polyoxyethylene diols, triols and tetrols such as the Carbowax™ polyols available from Union Carbide, Danbury, CT, the polyoxytetramethylenediols such as Polymeg™ polyols available from Quaker Oats Company, Chicago, IL, the polyester polyols such as the Multron™ poly(ethyleneadipate)polyols available from Mobay Chemical Company, and the polycaprolactone polyols such as the PCP™ polyols available from Union Carbide.

Examples of aromatic polyols include the polyester polyols that are prepared from aromatic dicarboxylic acids such as o-, m-, and p-phthalic acid and excess diols such as diethylene glycol, triethylene glycol, glycol, glycerine, and pentaerythritol; and from dicarboxylic acids such as adipic acid and resorcinol. Examples of monomeric polyols include resorcinol and o-, m-, and p-xylene-α,α'-diol.

Polyamines of Formula II can, for example, have a molecular weight of 60 to 2000 and include monomeric and polymeric primary and secondary aliphatic and aromatic amines having two to four amino groups. Examples include alkylene diamines such as ethylenediamine, triethylenetetraamine, diethylenetriamine, piperazine, as well as other polyamines such as the polyamines available from Jefferson Chemical Co., Inc., a subsidiary of Texaco, Inc., under the trade name Jeffamine™ such as Jeffamine™ D-400, a polyoxypropylene diamine having a molecular weight of about 400; Jeffamine™ D-230, a polyoxypropylene diamine having a molecular weight of about 230; Jeffamine™ T-403, a polyoxypropylene triamine having a molecular weight of about 400; and Jeffamine™ ED 600 and ED 900, which are polyoxyethylene diamines having molecular weights of 600 to 900, respectively. In addition, hydrazino compounds such as adipic dihydrazide or ethylene dihydrazine can be used, as can also, alkanolamines such as ethanolamine, diethanolamine, and tris(hydroxyethyl)ethylenediamine. The polymeric polyols and polyamines that have a molecular weight of 300 to 1000 are preferred.

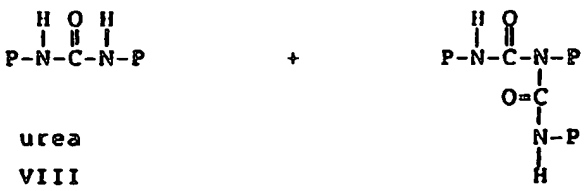
Sulfoarene- and sulfoalkanedicarboxylic acids of Formula I useful for preparation of the polyurethane/ polyurea sponges of the invention are any of the known sulfoarene- and sulfoalkanedicarboxylic acids. Examples of these include sulfoalkanedicarboxylic acids such as sulfosuccinic acid, 2-sulfoglutaric acid, 2,5-disulfoadipic acid, 2-sulfododecanedioic acid, sulfoarenedicarboxylic acids such as 5-sulfonaphthalene-1,4-dicarboxylic acid, 4,5-disulfonaphthalene-1,8-dicarboxylic acid, sulfobenzylmalonic acids such as those described in U.S. Patent No. 3,821,281; and sulfofluorenedicarboxylic acids such as 9,9-di(2'-carboxyethyl)fluorene-2-sulfonic acid described in British Patent No. 1,006,579. It is understood that the corresponding lower alkyl esters, halides, anhydrides, and salts of the above sulfonic acids can also be used in the preparation.

Polyisocyanates, Formula IV, that can be used to react with the sulfocompounds, Formula III, to form the isocyanate-terminated sulfocompounds that are intermediates to the polyurethane/polyurea sponges of the invention include any of the well-known polyisocyanates. Preferred polyisocyanates are hexamethylene diisocyanate, toluene diisocyanate, isophorone diisocyanate, 3,5,5-trimethyl-1-isocyanato-3-isocyanatomethylcyclohexane, 4,4'-diphenylmethane diisocyanate (MDI), 4,4'4"-triisocyanatotriphenylmethane, and the polymethylenepolyphenylisocyanates. Other polyisocyanates are well known and include those described in U.S. Patent Nos. 3,700,643 and 3,600,359 among many others. Mixtures of polyisocyanates can also be used such as the mixture of MDI and trimer of MDI available from Upjohn Polymer Chemicals as Isonate 143L™ "Liquid MDI".

It is also within the scope of the present invention to add up to 2 weight percent water with the polyisocyanate in step (b). The addition of water creates urea linkages in compounds V and Va.

The polyurethane/polyurea sponges of the invention can be provided by any of steps (c), (d), and (e). In step (c), preferably about 1 equivalent of isocyanate-terminated sulfocompound mixture comprising compounds of Formulae V, Va, and IV, is admixed with 1 to 50 moles of water. Preferably, 0.01 to 5.0 weight percent of a surfactant such as a nonionic alkylphenyl polyether alcohol (Pluronic L-64™, BASF Wyandotte Corp, Parsippany, NJ) and 0.0 to 2.0 weight percent of a catalyst such as N-ethylmorpholine (Texaco Chemical Co.) is added. Other useful catalysts include tin catalysts or urethane catalysts such as those available as DABCO™ (Air Products and Chemicals, Inc., Allentown, PA). Although a catalyst can be used in step (e), one generally is not needed. The catalyst preferably is added with the water, before admixing with the isocyanate-terminated sulfopolyurethane, to accelerate crosslinking of the resin and CO_2 evolution and to provide lower density and a more open structured sponge. Useful blowing agents include any gas or volatile organic compound that dissolves in the compound of Formula V, such as trichlorofluoromethane (Freon-113™, Dupont de Nemours Co., Wilmington, DE). The reaction mixture is subjected to high speed mechanical stirring, preferably for 20 to 30 seconds at about 800 rpm at ambient conditions, and then it is immediately poured into a flat vessel, whereupon an expansion of the resin takes place. In this expansion of the resin, carbon dioxide gas is released in a chemical reaction which causes a porous, open-cellular mass to form. The resulting sponge is trimmed to remove the outer skin and then is oven-cured at low temperatures (35 to 80°C, preferably about 50°C) for 0.5 to 6 hours, preferably about 2 hours.

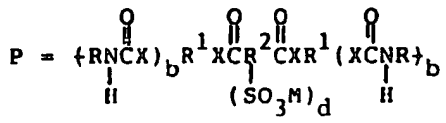
If the sponge is prepared via step (c) it can be one or more than one 3-dimensional crosslinked molecule having a plurality of units



urea
VIII

biuret
IX

wherein



and R, R^1, R^2, M, X, b and d are as defined above.

If the sponge is prepared via steps (d) or (e), the procedure is preferably modified as follows:

To about 1 mole of the isocyanate-terminated sulfopolyurethane/urea mixture of compounds of Formula V, Va, and IV, 0.8 to 1.2 moles of a polyol $R^3(OH)_c$ (Formula VI) or 0.5 to 1.5 moles of a polyamine $R^3(NH_2)_c$ (Formula VII) is added 1 to 20 weight percent (preferably 5 to 15 weight percent) of a blowing agent. The blowing agent is admixed using the procedure as for step (c). The reaction of step (d) preferably includes a catalyst and amount as described in step (b). Step (e) generally requires no catalyst. In steps (d) or (e) it may be advantageous to use an amount of water in addition to or instead of the blowing agent, i.e., 0.01 to 40.0 weight percent, to be added to the polyol or polyamine to augment or supply the necessary blowing agent.

Polyols, $R^3(OH)_c$, and polyamines, $R^3(NH_2)_c$ that can be used in steps (d) and (e) preferably are the aliphatic polyols and polyamines of Formula II. Aromatic polyamines such as 1,2-, 1,3-, and 1,4-phenylenediamine, toluenediamine and the like can be used in amounts generally up to 50% by weight. The sulfopolyols of Formula III can also be used in step (d).

In steps (c), (d), and (e) the product may comprise a mixture of polyurea (VIII) and/or (XI), polyurethane (X), and biuret units (IX).

A blowing agent is useful with the polyamine or polyol of reaction steps (d) or (e) in preparing the sponge of the invention. Useful blowing agents include C_1 to C_8 hydrocarbons, C_1 and C_2 chlorinated hydrocarbons such as meth-

ylene chloride, dichloroethene, monofluorotrichloromethane (Freon 113™, Dupont), difluorodichloromethane, acetone, as well as nonreactive gases such as carbon dioxide, nitrogen, or air.

As is known in the art, there can optionally be incorporated in the sponges during their preparation various adjuvants such as fillers and fibers (e.g., nylon, rayon, cellulose, polypropylene, diatomaceous clays and other inorganic fillers), deodorants, medicinals, insecticides, fungicides, antimicrobials, humectants, pigments, or dyes.

The polyurethane/polyurea sponges of the present invention exhibit water absorption rates equal to or better than cellulose sponges of comparable density, equivalent absorption capacity to cellulose sponges, and have dramatically reduced swell, i.e., swell in volume of less than 30% while cellulose sponges swell up to 60% or more. The sponges of the present invention find use in home and industrial applications including in nonwoven sponge laminates (e.g., comprising Scotchbrite™ sponge laminates, 3M, St. Paul, MN), sponge laminates to fabrics, synthetic chamois, personal care, and medical products.

In the Examples below the following test methods were used:

1. Procedure for Measurement of Percent Swell

A sponge sample approximately 5cm x 5cm x 0.6cm was oven dried at 64°C for 6 hours. The length, width, and thickness of the sponge were measured in order to calculate the dry volume. The sponge was then thoroughly saturated with water (approximately 1 hour soaking in water to permit total possible swell), wrung out, and the dimensions measured in order to calculate wet volume. The percent volume change (percent swell) was calculated by

$$\frac{\text{Vwet - Vdry}}{\text{Vdry}} \times 100 = \text{percent swell}$$

2. Procedure for Measurement of Rate of Absorption

A sponge sample of approximately 5cm x 5cm x 0.6cm was prepared by soaking in water for 1 hour prior to testing. The sponge was wrung out, weighed, and the length and width of this sponge were then measured. Rate of water absorption was measured in a water container equipped with a perforated metal plate placed 3mm below the water overflow level. Water was held constant at this level by a constant flow into the container; water was maintained at room temperature (about 21°C).

In order to measure rate, the sponge was placed on the surface of the perforated plate such that the measured area was in contact with the plate, and held in this position for exactly five seconds. The sponge was removed and weighed immediately to measure the amount of water absorbed. Rate of water absorption was then calculated by

$$\text{rate of absorption} = \frac{\text{net weight of water absorbed in 5 seconds}}{\text{cross sectional area}}$$

3. Procedure for Measuring Wet Wipe

A dry sponge was cut to provide a sample having the dimensions 7.6cm x 10.2cm x 1.3cm and squeezed under water at 21°C to remove air. The sample was then squeezed in air using a rubber roller wringer to remove excess water. The sponge was then weighed and the weight was recorded as M_1. Twenty grams of distilled water were poured onto the surface of a clean glass mirror and without applying pressure, the wrung out sponge sample was passed in five back and forth motions through the water. The sponge was then reweighed and the weight recorded as M_2.

$$\text{percent wiping capacity} = \frac{M_2 - M_1}{20} \times 100$$

Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention.

Example 1 - sulfocompound synthesis (step a)

A one liter flask was fitted with a mechanical stirrer, nitrogen purge, condenser and receiver for condensate. The flask was charged with 1.0 moles (600 g) ethyleneoxide polyol (Carbowax 600™, Union Carbide, Danbury, CT), 0.25 moles (24.0 g) dimethyl sodium 5-sulfoisophthalate (previously dried above 100 degrees C in a vacuum oven), and

100 g toluene. The flask was heated in a Woods metal bath to 130°C to distill toluene and thus dry the reactants. When all of the toluene was removed the reactants were heated to 200°C at which time 0.2 g $Zn(OAc)_2$ is added (0.03 wt%). Esterification accompanied by the evolution of methanol took place. The temperature was raised to 245°C for a period of 4 hours, at which time the pressure was reduced to 1 mm for 30 to 60 minutes. Hot resin was the poured into dry containers and capped under dry N_2 to prevent absorption of water. The OH equivalence of this diol was typically approximately 465 g/mole OH as determined by the NCO method.

Example 2 - isocyanate endcapping reaction (step b)

A two-liter flask was fitted with mechanical stirrer, addition funnel, dry nitrogen purge, and oil bath heating. The flask was charged with 500.0 g of a mixture of 4,4'-diphenylmethane diisocyanate-based polyisocyanates (Isonate 143L™, Upjohn, Kalamazoo, MI), and 0.58 g (0.05 wt %) ethanesulfonic acid (this acid was introduced slowly with rapid stirring). The temperature of this mixture was raised to 60°C, at which time the addition of 465.0 g of the sulfodiol prepared as in Example 1 was begun; the addition lasted approximately one hour, at a rate allowing a maximum exotherm of 80°C. When addition was complete the reaction was held at 70°C for 2 hours, at which time the resin was poured into predried containers under dry N_2. An isocyanate-terminated sulfopolyurethane having a typical NCO equivalence of 385 g/mole NCO was found to be present.

Example 3 - sponge forming reaction

70.0 g of the isocyanate-terminated sulfopolyurethane prepared as in Example 2 was weighed into a 500 ml plastic beaker. In a separate 50 ml beaker 30 g of water was mixed with 0.35 g nonionic alkylphenyl polyether alcohol surfactant (Pluronic L-64™) 0.53 g N-ethylmorpholine, and a water soluble dye (if desired). The two were mixed together with a high speed mechanical stirrer for 20 to 30 seconds at about 800 rpm, and then immediately poured into an aluminum pan before significant expansion of the resin occurred. CO_2 was released in a chemical reaction and caused a porous, open cellular mass to form. The resulting sponge was trimmed to remove the outer skin and it was then oven cured at 50°C for 2 hours. Performance of the resulting sponge designated 3A will be described in Example 4.

This example was repeated except that the mixing of the components with the high speed stirrer was for 30 to 40 seconds to provide a sponge designated 3B.

This example was repeated except that the mixing of the components with the high speed stirrer was for 10 to 20 seconds to provide a sponge designated 3C.

Example 4

Sponges of three different chemical compositions, some having similar densities, were evaluated for water absorption properties. The data is shown in TABLE I below.

TABLE I

Properties of Sponges				
	Density	Rate[c]	% Swell	Wet Wipe
Hypol-4000™[a]	0.0400	.002	40-60	45-50%
Cellulose[b]	0.0450	.017	30-60	90-95%
Sponge 3A of Example 3	0.0400	.017	15-25	90-95%
Sponge 3B of Example 3	0.0350	.018	15-25	-
Sponge 3C of Example 3	0.0835	.014	15-25	-

(a) non-ionic sponges based on polyethyleneoxide prepolymer available from W.R. Grace.

(b) Scotch Brite® Kitchen scrub sponge™ (3M, St. Paul, MN)

(c) rate of water absorption in g/cm^2 per 5 seconds

The data of TABLE I shows that the rate of water absorption and wet wipe of non-ionic sponges are low (0.002 g/cm^2 sec and 45 to 90% respectively) relative to cellulose sponges and the sponges of Example 3 (0.017 g/cm^2 sec and 90-95% respectively) and that the percentage swell of the sponges of Example 3 (15-25%) is dramatically lower than that of the non-ionic sponges (40-60%) and cellulose sponges (30-60%).

Example 5

A one liter flask equipped as described in Example 1 was charged with 1.67 moles (250.0 g) triethylene glycol (Aldrich), 1.11 moles (162.2 g) dimethyladipate (Aldrich), and 100 g toluene. The flask was heated in the Woods metal bath to 140°C to distill toluene and thus dry the reactants. There was then added 0.10 g zinc acetate. Heating was continued to a temperature of 200°C. Evolution of methanol took place indicating esterification of the triethylene glycol with adipic acid. There was then added 0.28 moles (82.2 g) dimethyl sodium 5-sulfoisophthalate (previously dried in a vacuum oven at 100°C) and 0.05 g zinc acetate. The temperature of the flask contents was then elevated to 250°C and held for a period of 5 hours. The pressure in the flask was then reduced to 1 mm for one hour to remove volatiles. Sulfopolyesterdiols obtained by this process typically had an hydroxyl equivalent weight of about 700 as determined by isocyanate titration.

The sulfopolyesterdiol, as obtained above (350 g) was isocyanate endcapped by reaction with 250 g of Isonate 143 L in accordance with the procedure of Example 2. An isocyanate-terminated sulfopolyesterpoly-urethane was obtained having an isocyanate equivalent weight of 580 was obtained.

A sponge prepared in accordance with the procedure of Example 3 using the above isocyanate-terminated sulfopolyesterpolyol had characteristics similar to those of the sponge of Example 3.

Examples 6-15

Sponges were prepared by the reaction according to the procedure described in Example 3 using the materials shown in Column A, as indicated in TABLE II. The isocyanate-terminated sulfocompound in Column A was prepared according to the procedure described in Example 2 using the moles of Isonate 143L™ to one mole of sulfocompound shown in Column B. The sulfocompounds in Column C were prepared according to the procedure described in Example 1 by reaction of one mole of dimethyl sodium isophthalate with the moles of polymeric diol shown in Column C.

The sulfocompound-containing sponges prepared as described in Examples 6-15 are hydrophilic and exhibit various densities, rates of water absorption, percentage swell and wet wipe characteristics.

TABLE II

	A				B	C	
	Sponge preparation				Preparation of its[h]	Preparation of sulfocompound	
Ex. No.	ITS[h] g	H_2O g	Surfactant[f] g	Catalyst[g] g	mole ratio[i]	Polyol	Mole ratio[j]
6	70	30	0.35	0.53	3.5	PEO[k] 600	4
7	70	20	0.50	0.50	3.1	PEG 400	4
8	70	24	0.40	0.70	3.5	PEO 600 and PEO 400	2 2
9	70	32	0	0	3.3	PEO 1000	4
10	70	35	0	0	3.5	PEO 1000 and PEO 1450	2 2
11	70	26	0	0	2.5	PEO 1000	4
12	70	30	0.30	0.80	3.5	Polyester diol[l]	2
13	70	30	0.35	0.70	3.5 (chain[m] extended with 5% butanediol)	PEO	4
14	70	30	0.35	0.70	3.5 (chain extended with 10% butanediol)	PEO 600	4
15	70	30	0.40	0.70	3.5 (chain extended with 5% tris-(hydroxyethyl)-isocyanurate	PEO 600	4

(f) Pluronic L-64
(g) N-ethylmorpholine
(h) isocyanato-terminated sulfocompound
(i) mole ratio of Isonate 143L™ to sulfocompound
(j) mole ratio of polyol to dimethylsodium 5-sulfoisophthalate
(k) polyethyleneoxy diols, PEO with molecular weight specified, (Carbowax™, Union Carbide)
(l) prepared as described in Example No. 5
(m) chain extension was done by heating at 60°C for one hour a mixture of the isocyanate-terminated sulfocompound and the chain extender

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Example 16-22

Sponges, as indicated in TABLE III, were prepared in accordance with step (d) by mixing 43 g of the isocyanate-terminated sulfocompound of Example 6 using a high speed mechanical stirrer for 20 to 30 seconds at about 800 rpm with the materials shown, pouring the mixture immediately into an aluminum pan, and placing the foaming mixture into an oven at 100°C where it is allowed to cure for 30 to 60 seconds and then removed from the oven.

TABLE III

					BLOWING AGENTS	
	ITS[n]	Curative[u]		Surfactants[s]	Water	Freon 113
Ex. No.	g	Polyol	Wt(g)	(g)	g	g
16	43	PCP-0200[p]	(18)	0.25	-	8
17	43	trimethylolpropane	(3)	0.25	5.0	8
18	43	castor oil	(11)	-	-	10[t]
19	43	triethyleneglycol	(7)	0.20	-	10
20	43	sulfocompound[q]	(23)	0.25	-	10[t]
21	43	butanediol	(3.0)	0.25	5.0	-
22	53[r]	butanediol	(4.5)	-	-	10

(n) isocyanate-terminated sulfocompound of Example 6
(p) polycaprolactonetriol (available from Union Carbide)
(q) the sulfoglycol of Example 7
(r) isocyanate-terminated sulfocompound of Example 9
(s) surfactant was Pluronic L-64
(t) blowing agent was pentane in place of Freon 113
(u) the catalyst used in each composition was 0.1 g dibutyltin dilaurate

It is to be observed that hydrophilic sponges prepared using a polyol curative in place of water can be made to have characteristics similar to those prepared using water as the curative for the isocyanate-terminated sulfocompound.

Examples 23-27

The procedure of Example 16-22 were repeated using as curative polyamines dissolved in water in place of the polyols. The materials used are shown in TABLE IV.

TABLE IV

	ITS[n]	Curative		Surfactant[s]	Catalyst[g]
Ex. No.	g	Polyamine[v]	Wt(g)	g	g
23	43	Jeffamine D-2000	2.0	-	-
24	43	Jeffamine D-2000	5.0	0.25	0.25
25	43	Jeffamine D-230	1.0	-	-
26	43	Jeffamine D-230	1.0	0.25	0.25
27	43	Jeffamine D-600	5.0	0.25	0.25

(n) isocyanate-terminated sulfocompound of Example No. 6.
(s) Pluronic L-64
(g) N-ethylmorpholine
(v) dissolved in 15g water

The hydrophilic sponges prepared using polyamines in place of water had characteristics similar to those prepared using polyols as curative. Similar sponges can be made using mixtures of polyols and polyamines as curatives.

Example 28

A two liter flask equipped as described in Example 1 was charged with 3.0 moles (450g) triethylene glycol, 1.0

mole (194g) dimethyl isophthalate, 1.0 mole (144g) dimethyl maleate, and 150g toluene. The flask was heated in the Woods metal bath to 140°C to distill toluene and thus dry the reactants. 0.2g zinc acetate was then added and heating was continued to a temperature of 200°C. Following the completion of methanol evolution 0.5 moles (148g) dimethyl sodium 5-sulfoisophthalate (previoulsy dried in a vacuum oven at 100°C) and 0.05g zinc acetate were added to the flask. The temperature of the flask contents was then elevated to 250°C and held for a period of 5 hours. The pressure in the flask was then reduced to 1 mm for 1 hour to remove volatiles. Sulfodiols obtained by this process typically have a hydroxyl equivalent weight of about 660 as determined by isocyanate titration.

The sulfopolyesterdiol as obtained above (780g) was mixed with 1 mole (600g) of Carbowax 600 and endcapped with 1502g of Isonate 143L in accordance with the procedure of Example 2. An isocyanate-terminated sulfopolyesterpolyurethane was thus obtained having an isocyanate equivalent weight of 480-500.

A sponge prepared in accordance with the procedure of Example 3 using the above isocyanate-terminated sulfopolyesterpolyol had characteristics similar to those of the sponge in Example 3.

Example 29

The sulfodiol (419g) prepared as in Example 1 was mixed with 4.5g trimethylol propane, and then endcapped with 500g of Isonate 143L according to the procedure of Example 2. The resulting sulfopolyurethane was foamed according to the procedure of Example 3 giving a hydrophilic, resilient, open celled foam.

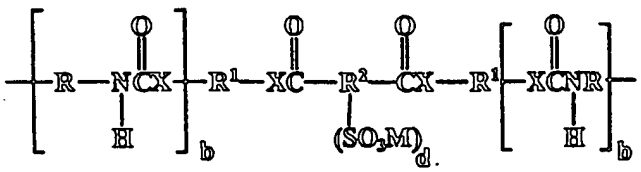
Example 30 - isocyanate endcapping reaction (step b)

A two-liter flask was fitted with mechanical stirrer, addition funnel, dry nitrogen purge, and oil bath heating. The flask was charged with 500.0 g of a mixture of 4,4'-diphenylmethane diisocyanate-based polyisocyanates (Isonate 143L™, Upjohn, Kalamazoo, MI), and 0.58 g (0.05 wt %) ethanesulfonic acid (this acid was introduced slowly with rapid stirring). The temperature of this mixture was raised to 60°C, at which time the addition of 465.0 g of the sulfodiol prepared as in Example 1 and 2.3 g water was begun; the addition lasted approximately one hour, at a rate allowing a maximum exotherm of 80°C. When addition was complete the reaction was held at 70°C for 2 hours, at which time the resin was poured into predried containers under dry N_2. An isocyanate-terminated sulfooclyurethane/urea having a typical NCO equivalence of 430 g/mole NCO was found to be present.

A sponge prepared in accordance with the procedure of Example 3 using the above isocanate-terminated sulfopolyurethane/urea had characteristics similar to those of the sponge in Example 3.

Claims

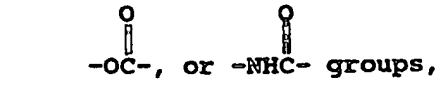
1. A hydrophilic water-absorbing sponge comprising a polymer of urea and/or urethane and incorporating at least one sulfonate equivalent per 20,000 molecular weight units, characterized in that the polymer comprises a plurality of units having the formula



wherein

R is an organic group having a valence of 2, 3 or 4 selected from linear and branched aliphatic groups having 2 to 12 carbon atoms, and 5- and 6-membered aliphatic and aromatic carbocyclic groups having 5 to 50 carbon atoms;

each R^1 is independently a linear or branched organic group having a valence of (b + 1) consisting of a chain of up to 110 carbon atoms in units selected from linear groups C_nH_{2n} and C_nH_{2n-2} in which n is 2 to 12, 5- or 6-membered carbocyclic groups, and aromatic groups of 5 to 20 carbon atoms, which are separated by ether oxygen atoms, or



the linear or branched organic group having a molecular weight of up to 2000, wherein b is an integer of 1, 2 or 3; and

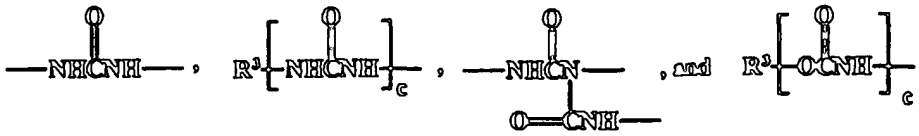
R^2 has a valence of d + 2 and is an arenepolyyl group (polyvalent arene group) having 6 to 20 carbon atoms or an alkanepolyyl (polyvalent alkane) group having 2 to 20 carbon atoms,

wherein d is a number 1, 2 or 3,

X is independently -O- or -NH-, and

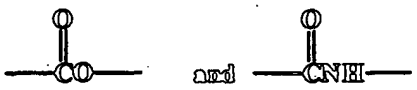
M is a cation.

2. A sponge according to claim 1 further comprising a plurality of units selected from the group consisting of



wherein

R^3 is a linear or branched aliphatic group having 2 to 50 carbon atoms or an aromatic group of 5 to 50 carbon atoms having a valence of c in which c is a number having a value of 2 to 5, the group optionally containing 1 to 20 nonperoxidic oxygen atoms,



groups or R^3 is a 5- or 6-membered cycloaliphatic group or aromatic group having 5 to 20 carbon atoms.

3. A sponge according to claim 1 having an absorptive capacity of 10 to 50 grams of water per gram of dry sponge.

4. A sponge according to claim 1 having a rate of water absorption of 0.001 to 0.04 g/cm^2/5 sec.

5. A sponge according to claim 1 having a density in the range of 0.01 to 0.4 g/cm^3.

6. A sponge according to claim 1 having a percentage volumetric swell in water of 25 to 50%.

7. A sponge according to claim 1 having a percentage volumetric swell in water of less than 30%.

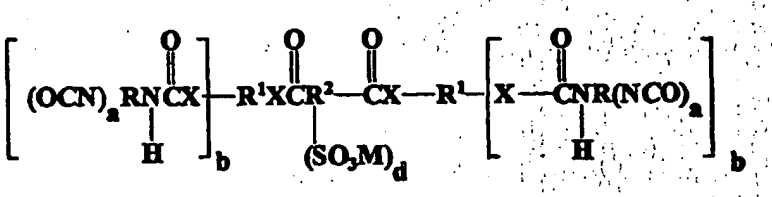
8. A sponge according to claim 2 or claim 3 wherein M is H, an alkali or alkaline earth metal cation, or a primary, secondary, tertiary, or quarternary ammonium cation.

9. A sponge according to any preceding claim further comprising adjuvants selected from the class consisting of fibers, fillers, deodorants, medicinals, insecticides, fungicides, antimicrobials, humectants, pigments, or dyes.

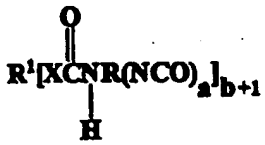
10. A sponge according to any preceding claim wherein said polymer contains one sulfonate equivalent per 3,000 to 10,000 molecular weight units.

11. A method of preparing a sponge comprising the steps of

(a) providing an isocyanate-terminated sulfopolyurethane/urea comprising a compound having the formula



and, optionally, at least one of compounds having the formulae $OCNR(NCO)_a$ and



wherein a is an integer of 1 to 3, b is an integer of 1 to 3, and
R, R^1, R^2, X and M are as defined in claim 1;
b) reacting said sulfopolyurethane/urea with at least one of

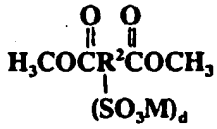
(a) water, and
(b) at least one of a polyol or polyamine plus a blowing agent, and

c) isolating the resulting sponge,

said sponge incorporating at least one sulfonate equivalent per 20,000 molecular weight.

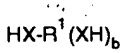
12. A method according to claim 11 wherein said isocyanate-terminated sulfopolyurethane/urea is formed by:

a) reacting a sulfodicarboxylic ester of formula:



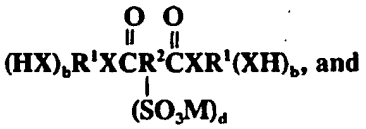
(I)

with a polyol or polyamine of formula:



(II)

to form a compound of formula:



(III)

b) reacting said compound of step a) with a polyisocyanate of formula:

$$OCNR(NCO)_a \qquad (IV)$$

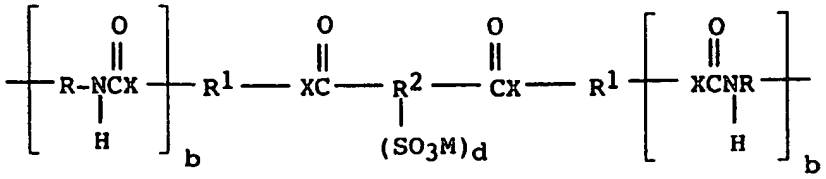
wherein a is an integer of 1 to 3 and R, R^1, R^2, M, b and d are as defined in claim 1.

13. A method according to claim 11 or claim 12 wherein said polyol or polyamine has the formula $R^3(OH)_c$ or $R^3(NH_2)_c$ respectively wherein R^3 and c are as defined in claim 2.

14. Use of a sponge as claimed in any of claims 1 to 10 to absorb an aqueous liquid.

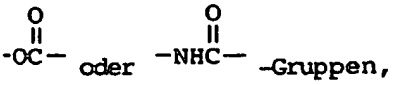
Patentansprüche

1. Hydrophiler, wasserabsorbierender Schwamm, umfassend ein Polymer aus Harnstoff und/oder Urethan und inkorporierend mindestens ein Sulfonat-Äquivalent pro 20.000 Molekular-Einheiten, dadurch gekennzeichnet, daß das Polymer eine Vielzahl von Einheiten der Formel aufweist:



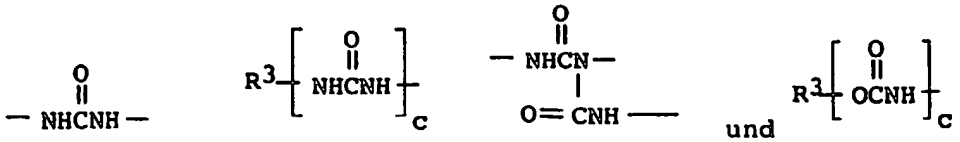
worin sind:

R eine organische Gruppe mit einer Wertigkeit von 2, 3 oder 4, ausgewählt aus linearen und verzweigten aliphatischen Gruppen mit 2 ... 12 Kohlenstoffatomen und 5- und 6-gliedrigen aliphatischen und aromatischen, carbocyclischen Gruppen mit 5 ... 50 Kohlenstoffatomen;
jedes R^1 unabhängig eine lineare oder verzweigte organische Gruppe mit einer Wertigkeit von (b + 1), bestehend aus einer Kette mit bis zu 110 Kohlenstoffatomen in Einheiten, ausgewählt aus linearen Gruppen C_nH_{2n} und C_nH_{2n-2}, worin n 2 ... 12 ist, 5- oder 6-gliedrigen carbocyclischen Gruppen und aromatischen Gruppen mit 5 ... 20 Kohlenstoffatomen, die durch Ether-Sauerstoffatome separiert sind, oder



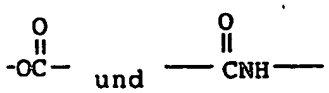
die linearen oder verzweigten organischen Gruppen mit einer relativen Molekülmasse bis zu 2.000, worin b eine ganze Zahl von 1, 2 oder 3 ist; sowie
R^2 mit einer Wertigkeit von d+2 eine Arenpolyyl-Gruppe (mehrwertige Aren-Gruppe) mit 6 ... 20 Kohlenstoffatomen oder eine Alkanpolyyl-Gruppe (mehrwertige Alkan-Gruppe) mit 2 ... 20 Kohlenstoffatomen, worin d eine Zahl von 1, 2 oder 3 ist;
X unabhängig -O- oder -NH-, sowie
M ein Kation.

2. Schwamm nach Anspruch 1, ferner umfassend eine Vielzahl von Einheiten, ausgewählt aus der Gruppe, bestehend aus



worin sind:

R^3 eine lineare oder verzweigte aliphatische Gruppe mit 2 bis 50 Kohlenstoffatomen oder eine aromatische Gruppe mit 5 bis 50 Kohlenstoffatomen mit einer Wertigkeit von c, worin c eine Zahl mit einem Wert von 2 ... 5 ist, welche Gruppe wahlweise 1 ... 20 nichtperoxidische Sauerstoffatome enthält,



Gruppen oder R^3 ist eine 5- oder 6-gliedrige cycloaliphatische Gruppe oder eine aromatische Gruppe mit 5 bis 20 Kohlenstoffatomen.

3. Schwamm nach Anspruch 1 mit einem Absorptionsvermögen von 10 ... 50 g Wasser pro Gramm trockener Schwamm.

4. Schwamm nach Anspruch 1 mit einer Geschwindigkeit der Wasserabsorption von 0,001 ... 0,04 g/cm^2 und 5 Sekunden.

5. Schwamm nach Anspruch 1 mit einer Dichte im Bereich von 0,01 ... 0,4 g/cm^3.

6. Schwamm nach Anspruch 1 mit einem relativen Volumen-Quellvermögen in Wasser von 25 ... 50 %.

7. Schwamm nach Anspruch 1 mit einem relativen Volumen-Quellvermögen in Wasser von weniger als 30 %.

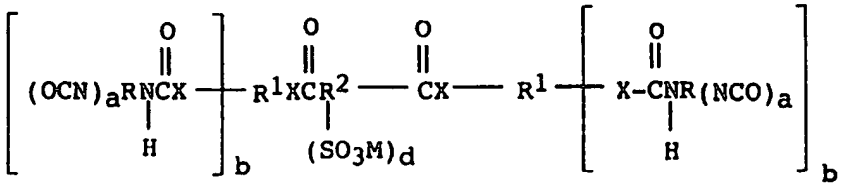
8. Schwamm nach Anspruch 2 oder 3, bei welchem M Wasserstoff, ein Alkali- oder Erdalkalimetall-Kation oder ein primäres, sekundäres, tertiäres oder quaternäres Ammonium-Kation ist.

9. Schwamm nach einem der vorgenannten Ansprüche, ferner umfassend Adjuvantien, ausgewählt aus der Klasse, bestehend aus Fasern, Füllstoffen, Deodorantien, medizinischen Substanzen, Insektiziden, Fungiziden, antimikrobiellen Substanzen, Feuchthaltemitteln, Pigmenten oder Farbstoffen.

10. Schwamm nach einem der vorgenannten Ansprüche, bei welchem das Polymer ein Sulfonat-Äquivalent pro 3.000 ... 10.000 Molekular-Einheiten enthält.

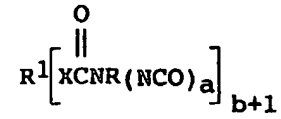
11. Verfahren zum Herstellen eines Schwammes, umfassend die Schritte:

(a) Bereitstellen eines Isocyanat-terminierten Sulfopolyurethan/Harnstoffes, umfassend eine Verbindung der Formel:



sowie wahlweise mindestens eine Verbindung mit den Formeln:

$OCNR(NCO)_a$ und



worin a eine ganze Zahl von 1 ... 3, b eine ganze Zahl von 1 ... 3 und R, R^1, R^2, X und M wie in Anspruch 1 festgelegt sind;
(b) Umsetzen des Sulfopolyurethan/Harnstoffes mit mindestens einem der folgenden:

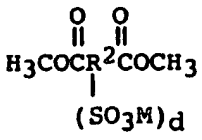
(a) Wasser,
(b) mindestens einem Polyol oder Polyamin plus einem Blähmittel und

(c) Isolieren des resultierenden Schwammes,

welcher Schwamm mindestens ein Sulfonat-Äquivalent pro 20.000 Molekular-Einheiten inkorporiert.

12. Verfahren nach Anspruch 11, bei welchem der Isocyanat-terminierte Sulfopolyurethan/Harnstoff erzeugt wird durch:

(a) Umsetzen eines Sulfodicarbonsäureesters der Formel:

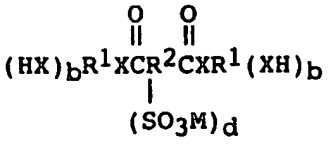


(I)

mit einem Polyol oder Polyamin der Formel:

$$HX\text{-}R^1(XH)_b \qquad \text{(II)}$$

um eine Verbindung der Formel zu erzeugen:



(III)

(b) Umsetzen dieser Verbindung von Schritt (a) mit einem Polyisocyanat der Formel:

$$OCNR(NCO)_a \qquad \text{(IV)}$$

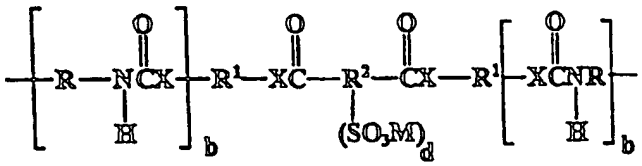
worin a eine ganze Zahl von 1 ... 3 ist und R, R^1, R^2, M, b und d wie in Anspruch 1 festgelegt sind.

13. Verfahren nach Anspruch 11 oder 12, bei welchem das Polyol oder Polyamin die Formeln $R^3(OH)_c$ bzw. $R^3(NH_2)_c$ haben und worin R^3 und c wie in Anspruch 2 festgelegt sind.

14. Verwendung eines Schwammes nach einem der Ansprüche 1 bis 10 zum Absorbieren einer wäßrigen Flüssigkeit.

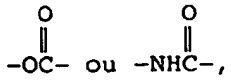
Revendications

1. Eponge hydrophile absorbant l'eau, comprenant un polymère d'urée et/ou d'uréthane et incorporant au moins un équivalent de sulfonate pour 20 000 unités de poids moléculaire, caractérisée en ce que le polymère comprend une pluralité d'unités ayant la formule



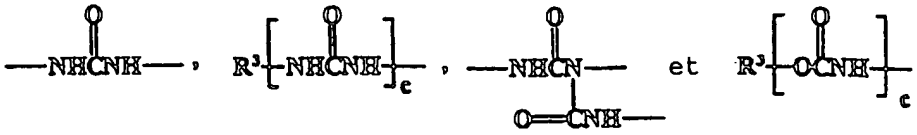
où

R est un groupe organique ayant une valence de 2, 3 ou 4, choisi parmi les groupes aliphatiques linéaires ou ramifiés ayant de 2 à 12 atomes de carbone, et les groupes carbocycliques à 5 ou 6 chaînons, aliphatiques ou aromatiques, ayant de 5 à 50 atomes de carbone ;
chaque R^1 est indépendamment un groupe organique linéaire ou ramifié ayant une valence de (b + 1), constitué d'une chaîne ayant jusqu'à 110 atomes de carbone dans des unités choisies parmi les groupes linéaires C_2H_{2n} et C_2H_{2n-2}, où n vaut de 2 à 12, les groupes carbocycliques à 5 ou 6 chaînons, et les groupes aromatiques ayant de 5 à 20 atomes de carbone, qui sont séparés par des atomes d'oxygène en fonction éther ou des groupes



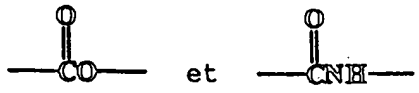
le groupe organique linéaire ou ramifié ayant un poids moléculaire allant jusqu'à 2 000, où b est un nombre entier de 1, 2 ou 3 ; et
R^2 a une valence de d + 2 et est un groupe arylène-polyyle (groupe arène polyvalent) ayant de 6 à 20 atomes de carbone ou un groupe alcanepolyyle (alcane polyvalent) ayant de 2 à 20 atomes de carbone,
où d est un nombre valant 1, 2 ou 3,
X est indépendamment -O- ou -NH-, et
M est un cation.

2. Eponge selon la revendication 1, comprenant, en outre, une pluralité d'unités choisies dans l'ensemble constitué par



où

R^3 est un groupe aliphatique linéaire ou ramifié ayant de 2 à 50 atomes de carbone ou un groupe aromatique ayant de 5 à 50 atomes de carbone, ayant une valence de c, où c est un nombre ayant une valeur de 2 à 5, ce groupe contenant éventuellement de 1 à 20 atomes d'oxygène non-peroxydique, des groupes



ou R^3 est un groupe cycloaliphatique à 5 ou 6 chaînons ou un groupe aromatique ayant de 5 à 20 atomes de carbone.

3. Eponge selon la revendication 1, ayant une capacité d'absorption de 10 à 50 grammes d'eau par gramme d'éponge sèche.

4. Eponge selon la revendication 1, ayant une vitesse d'absorption d'eau de 0,001 à 0,04 g/cm^2/5 secondes.

5. Eponge selon la revendication 1, ayant une densité comprise entre 0,01 et 0,4 g/cm^3.

6. Eponge selon la revendication 1, ayant un pourcentage de gonflement volumétrique dans l'eau de 25 à 50 %.

7. Eponge selon la revendication 1, ayant un pourcentage de gonflement volumétrique dans l'eau inférieur à 30 %.

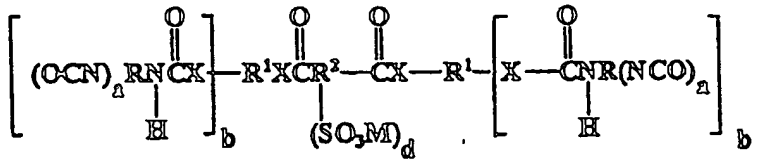
8. Eponge selon la revendication 2 ou 3, où M est H, un cation de métal alcalin ou alcalino-terreux, ou un cation ammonium primaire, secondaire, tertiaire ou quaternaire.

9. Eponge selon l'une quelconque des revendications précédentes, comprenant, en outre, des adjuvants choisis dans la classe constituée par les fibres, les charges, les déodorants, les substances médicamenteuses, les insecticides, les fongicides, les agents antimicrobiens, les agents hydratants, les pigments ou les colorants.

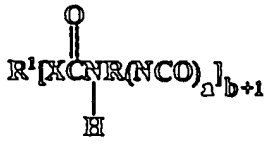
10. Eponge selon l'une quelconque des revendications précédentes, dans laquelle ledit polymère contient un équivalent de sulfonate pour 3 000 à 10 000 unités de poids moléculaire.

11. Procédé de préparation d'une éponge, comprenant les étapes consistant à :

a) fournir un composé sulfopolyuréthane/urée à terminaison isocyanate, comprenant un composé ayant la formule



et éventuellement au moins un des composés ayant une des formules $OCNR(NCO)_a$ et



où a est un nombre entier de 1 à 3, b est un nombre entier de 1 à 3, et R, R^1, R^2, X et M sont tels que définis dans la revendication 1 ;

b) faire réagir ledit composé sulfopolyuréthane/urée avec au moins :

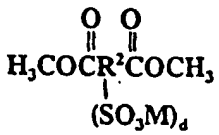
(a) de l'eau, et
(b) au moins un polyol ou une polyamine plus un agent de gonflement, et

c) isoler l'éponge résultante,

ladite éponge renfermant au moins un équivalent de sulfonate pour 20 000 unités de poids moléculaire.

12. Procédé selon la revendication 11, dans laquelle le composé sulfopolyuréthane/urée à terminaison isocyanate est formé par :

a) mise en réaction d'un ester sulfodicarboxylique de formule :

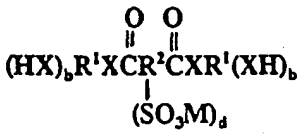


(I)

avec un polyol ou une polyamine de formule :

$$HX\text{-}R^1(XH)_b \qquad (II)$$

pour former un composé de formule :



(III)

et
b) mise en réaction dudit composé de l'étape a) avec un polyisocyanate de formule :

$$OCNR(NCO)_a \qquad (IV)$$

où a est un nombre entier de 1 à 3, et R, R^1, R^2, M, b et d sont tels que définis dans la revendication 1.

13. Procédé selon la revendication 11 ou la revendication 12, dans lequel ledit polyol et ladite polyamine répondent respectivement à la formule $R^3(OH)_c$ ou $R^3(NH_2)_c$, où R^3 et c sont tels que définis dans la revendication 2.

14. Utilisation d'une éponge selon l'une quelconque des revendications 1 à 10 pour absorber un liquide aqueux.